

DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/114,376 filed on December 30, 1998.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 15th day of February, 1999

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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Ammonia for Use in Manufacture of GaN-Type Compound Semiconductor and Method for Manufacturing GaN-Type Compound Semiconductor

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] Ammonia for use in the manufacture of a GaN-type compound semiconductor, being filled in a charging container in which at least a part of the ammonia is liquid and said liquid phase ammonia has a water concentration determined by a Fourier-transform infrared spectroscopy (FT-IR) of 0.5 vol ppm or less.

[Claim 2] A method for manufacturing a GaN-type compound semiconductor, comprising introducing the ammonia for the manufacture of a GaN-type compound semiconductor described in claim 1 in the gaseous state into a reaction chamber housing therein a substrate, and forming a layer comprising a GaN-type compound started from the ammonia on the substrate.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to ammonia for use in the manufacture of a GaN-type compound semiconductor and a method for producing a GaN-type compound semiconductor

using the ammonia.

[0002]

[Background Art]

Fig. 3 shows an example of conventional GaN-type compound semiconductor devices. The GaN-type compound semiconductor device shown here has a constitution such that a buffer layer 2 comprising $\text{Ga}_x\text{Al}_{1-x}\text{N}$ (wherein $0 \leq x \leq 1$) which is a GaN-type compound, an Si-doped n-type $\text{Ga}_x\text{Al}_{1-x}\text{N}$ layer (n-type clad layer) 3 which is an n-type clad layer doped with Si, a Zn-doped $\text{Ga}_x\text{Al}_{1-x}\text{N}$ layer (active layer) 4 which is a light emitting active layer doped with Zn, and an Mg-doped p-type $\text{Ga}_x\text{Al}_{1-x}\text{N}$ layer (p-type clad layer) 5 which is a p-type clad layer doped with Mg are laminated in sequence on a sapphire substrate 1 and electrodes 6 and 7 are provided on the n-type clad layer 3 and p-type clad layer 5, respectively.

This GaN-type compound semiconductor device can be used as a blue light emitting diode.

[0003]

Figs. 1 and 2 show an example of a production apparatus for use in the manufacture of the above-described GaN-type compound semiconductor device.

The production apparatus shown here is a metal-organic chemical vapor deposition (MOCVD) reactor and comprises a reaction chamber 11 for housing a sapphire substrate, a

support part 12 for holding the sapphire substrate in the reaction chamber 11, a heater 13 for heating the sapphire substrate supported by the support part 12, organic metal containers 14 and 15 as supply sources of organic metals, organic metal gas inlet tubes 16 and 17 for introducing organic metal gases supplied from the containers 14 and 15 into the reaction chamber 11, an ammonia charging container 18 as a supply source of ammonia gas, an ammonia gas inlet tube 19 for introducing the ammonia gas supplied from the charging container 18 into the reaction chamber 11, an outlet tube 20 for discharging gases in the reaction chamber 11 outside, an Si compound container 23, a Zn compound container 24, an Mg compound container 25, and inlet tubes 26, 27 and 28 for introducing the compounds supplied from the containers 23, 24 and 25 into the reaction chamber 11.

[0004]

The epitaxial wafer for use in the manufacture of the GaN-type compound semiconductor device is manufactured using the above-described production apparatus according to the MOCVD process as described below.

In the production of the GaN-type compound semiconductor device, a sapphire substrate 1 is housed in a reactor 11, an organic gallium housed in a container 14 and an organic aluminum housed in a container 15 are bubbled

with H₂ gas using tubes 21 and 22, the organic gallium gas and organic aluminum gas obtained are introduced together with H₂ gas into the reaction chamber 11 through inlet tubes 16 and 17, at the same time, an ammonia gas supplied from a charging container 18 is introduced into the reaction chamber 11 through an inlet tube 19, and then a buffer layer 2 comprising Ga_xAl_{1-x}N is formed on the surface of the sapphire substrate 1 using these organic gallium gas, organic aluminum gas and ammonia gas as raw materials.

[0005]

Subsequently, a Si compound supplied from a container 23 is fed into the reaction chamber 11 through a tube 26 together with the above-described organic gallium, organic aluminum and ammonia gas to form an n-type clad layer 3 on the buffer layer 2.

Then, a Zn compound supplied from a container 24 is fed into the reaction chamber 11 through a tube 27 together with the above-described organic gallium, organic aluminum and ammonia gas to form an active layer 4 on the n-type clad layer 3.

Thereafter, a Mg compound supplied from a container 25 is fed into the reaction chamber 11 through a tube 28 together with the above-described organic gallium, organic aluminum and ammonia gas to form a p-type clad layer 5 on the active layer 4.

The thus-manufactured epitaxial wafer is taken out from the reaction chamber 11 and electrodes 6 and 7 are provided on the n-type and p-type clad layers 3 and 5, respectively, thereby obtaining a GaN-type compound semiconductor device.

[0006]

[Problems to be Solved by the Invention]

The above-described conventional technique is, however, disadvantageous in that the GaN-type compound semiconductor device obtained is not likely satisfied in the light emitting property, particularly brightness. Accordingly, a technique capable of producing a GaN-type compound semiconductor device having excellent light emitting property without failure has been demanded.

The present invention has been made under these circumstances, and the object of the present invention is to provide a method for manufacturing a GaN-type compound semiconductor, where a GaN-type compound semiconductor having excellent light emitting property can be manufactured without fail.

[0007]

[Means to Solve the Problems]

The present inventors have found that the water concentration in the ammonia gas used as a raw material in the manufacture of GaN-type compound semiconductors has a

great effect on the light emitting property such as brightness of the GaN-type compound semiconductor. The present invention has been accomplished based on this finding.

More specifically, the ammonia for use in the manufacture of a GaN-type compound semiconductor of the present invention is filled in a charging container such that at least a part of the ammonia is liquid, and the liquid phase ammonia has a water concentration determined by a Fourier-transform infrared spectroscopy (FT-IR) of 0.5 vol ppm or less.

Furthermore, the method for producing a GaN-type compound semiconductor of the present invention comprises introducing the above-described ammonia in the gaseous state into a reaction chamber housing therein a substrate, and forming a layer comprising a GaN-type compound started from the ammonia on the substrate.

[0008]

[Mode for Carrying Out the Invention]

One practical embodiment of the method for producing a GaN-type compound semiconductor according to the present invention is described below by referring to the case where a production apparatus shown in Figs. 1 and 2 is used and a GaN-type compound semiconductor device shown in Fig. 3 is manufactured.

In the production apparatus for use in the manufacturing method of this embodiment, the ammonia in the charging container 18 is filled such that at least a part of the ammonia is liquid and the liquid phase ammonia has a water concentration determined by a Fourier-transform infrared spectroscopy (FT-IR) of 0.5 vol ppm or less.

The liquid phase ammonia preferably has a water concentration of 0.4 vol ppm or less, more preferably 0.2 vol ppm or less.

If the water concentration exceeds 0.5 vol ppm, the GaN-type compound semiconductor using the above-described ammonia is liable to be reduced in the light emitting properties such as brightness.

[0009]

The charging container 18 may be, for example, a cylindrical charging container shown in Figs. 1 and 2. The inner surface of the charging container is preferably subjected to plating or polishing treatment. The constructive material of the charging container 18 may be a manganese steel or aluminum alloy.

In the above-described ammonia, the concentration of residual impurities other than water is preferably 1 vol ppm or less.

[0010]

The above-described ammonia for the manufacture of a

GaN-type compound semiconductor can be produced, for example, by a method where crude ammonia is contacted with an adsorbent such as synthetic zeolite or zirconium oxide to adsorb water in the crude ammonia to the adsorbent or is superfractionated and the ammonia after the adsorption or distillation treatment is filled in the charging container 18.

At this time, it is preferred to prevent mixing of water to the utmost in respective processes after the adsorption or distillation treatment until the ammonia is filled in the charging container 18 and previously clean the charging container with purified ammonia or evacuate the charging container.

[0011]

In the manufacturing method of this embodiment, the GaN-type compound semiconductor is produced using the above-described ammonia for the manufacture of a GaN-type compound semiconductor as follows.

A sapphire substrate 1 is housed in a reaction chamber 11 and supported by a support part 12, the reaction chamber 11 is evacuated, and then the sapphire substrate 1 is heated using a heater 13 preferably at about 400°C.

Subsequently, an organic gallium such as trimethyl gallium (TMGa) housed in a container 14 and an organic aluminum such as trimethyl aluminum (TMAl) housed in a

container 15 are bubbled with H₂ gas using tubes 21 and 22, and the organic gallium gas and organic aluminum gas obtained are introduced together with H₂ gas into the reaction chamber 11 through inlet tubes 16 and 17.

At the same time, an ammonia gas supplied from a charging container 18 is introduced into the reaction chamber 11 through an inlet tube 19 to form a buffer layer 2 comprising Ga_xAl_{1-x}N started from these organic gallium gas, organic aluminum gas and ammonia gas, on the surface of the sapphire substrate 1.

[0012]

Then, the temperature of the substrate 1 is elevated to about 1,150°C and a Si compound such as silane supplied from a container 23 is fed together with the organic gallium gas, organic aluminum gas and ammonia gas into the reaction chamber 11 through a tube 26 to form a n-type clad layer 3 on the buffer layer 2.

Thereafter, a Zn compound such as dimethylzinc supplied from a container 24 is fed together with the organic gallium, organic aluminum and ammonia gas into the chamber 11 through a tube 27 to form an active layer 4 on the n-clad layer 3.

Furthermore, a Mg compound such as biscyclopentadienyl magnesium supplied from a container 25 is fed together with the organic gallium gas, organic aluminum gas and ammonia

gas into the reaction chamber 11 through a tube 28 to form a p-type clad layer 5 on the active layer 4.

After then, the thus-manufactured epitaxial wafer is taken out from the reaction chamber 11 and electrodes 6 and 7 are provided on the above-described n-type and p-type clad layers 3 and 5, respectively, to obtain the above-described GaN-type compound semiconductor device.

[0013]

According to the manufacturing method of this embodiment, the GaN-type compound semiconductor device obtained exhibits excellent light emitting property such as brightness. By virtue of this, the production yield can be improved.

[0014]

The reason why the GaN-type compound semiconductor device obtained by this manufacturing method exhibits excellent light emitting property is considered as follows. By setting the water concentration in the above-described ammonia to fall within the above-described range, the amount of oxygen mixed into the n-type and p-type clad layers 3 and 5 and the active layer 4, which are formed using the ammonia as a starting material, can be reduced and the layers each comprising such a GaN-type compound semiconductor can be prevented from deterioration in the crystallinity.

[0015]

In the embodiment described above, a method of forming n-type and p-type clad layers 3 and 5 and an active layer 4 each mainly comprising $\text{Ga}_x\text{Al}_{1-x}\text{N}$ started from the above-described ammonia is described. However, the present invention is not limited thereto and the above-described ammonia may be used for the manufacture of a GaN-type compound semiconductor where layers comprising a GaN-type compound such as GaN, InGaN, InGaAlN or AlGaN, are formed on a substrate.

[0016]

[Examples]

The present invention is described in greater detail below by specifically referring to the Examples.

(Test Example 1)

A GaN-type compound semiconductor device shown in Fig. 4 was manufactured as follows.

The ammonia charging container used here had a volume of 10 ℥ and was filled with 5 kg of liquefied ammonia. The charging container was used by placing it in a room temperature (24°C) condition.

[0017]

A circular sapphire substrate 1 having a diameter of 50 mm and a thickness of 0.3 mm was used after the surface thereof was specularly polished.

A single crystalline sapphire substrate 1 having a c face as the main plane was subjected to organic cleaning and supported on a support part in a reaction chamber. Then, the pressure in the reaction chamber was reduced to 1×10^{-3} torr or less, H₂ was introduced into the reaction chamber to return the pressure in the reaction chamber to the atmospheric pressure (760 torr), and the substrate temperature was raised to 1,150°C while introducing H₂ into the reaction chamber at 5 slm (standard l/min.), thereby thermal-cleaning the sapphire substrate 1.

[0018]

After lowering the substrate temperature to 450°C, a carrier gas comprising H₂ and N₂, ammonia gas and H₂ containing trimethyl aluminum (TMAI) vapor were fed into the reaction chamber at 6 slm, 1 slm and 20 sccm (standard cc/min.), respectively, over 1.5 minutes. At this time, the amount in mol of TMAI supplied was 3.8×10^{-5} mol/min.

During this process, a buffer layer 31 having a thickness of about 20 nm and comprising AlN was formed on the sapphire substrate 1.

[0019]

Thereafter, the supply of TMAI was stopped, the temperature of the sapphire substrate 1 was raised to 1,100°C, and while keeping this temperature, the above-described carrier gas, ammonia gas, disilane (Si₂H₆) diluted

with H₂ to 1 vol ppm, and H₂ containing trimethyl gallium (TMGa) vapor were fed into the reaction chamber at 6 slm, 2.5 slm, 5 sccm and 15 sccm, respectively, over 90 minutes. At this time, the amount in mol of TMGa supplied was 5.8×10^{-5} mol/min.

During this process, a n-type GaN layer 32 having a thickness of about 1.5 μm and a carrier concentration of about $3 \times 10^{17}/\text{cm}^3$ was formed.

[0020]

Subsequently, the supply of TMGa was stopped, the temperature of the sapphire substrate 1 was lowered to 850°C, and while keeping this temperature, the carrier gas, ammonia gas, diethylzinc (DEZn) diluted with hydrogen to 100 vol ppm, Si₂H₆ diluted with H₂ to 1 vol ppm, H₂ containing TMGa vapor, and H₂ containing trimethylindium (TMIn) vapor were fed into the reaction chamber at 6 slm, 2.5 slm, 10 sccm, 10 sccm, 5 sccm and 13 sccm, respectively, over 15 minutes. At this time, the amounts in mol of TMGa and TMIn supplied were 1.9×10^{-5} mol/min and 7.6×10^{-5} mol/min, respectively.

During this process, an InGaN active layer 33 having a thickness of about 100 nm and containing Si and Zn impurities was formed.

[0021]

Then, while keeping the sapphire substrate 1 at the

same temperature as in the formation of the InGaN active layer, the supply of TMIn was stopped and the carrier gas, ammonia gas and H₂ containing TMGa vapor were fed into the reaction chamber at 6 slm, 4.5 slm and 1 sccm, respectively, over 2 minutes. At this time, the amount in mol of TMGa supplied was 3.8×10^{-6} mol/min.

During this process, a GaN layer 34 having a thickness of about 3 nm was formed.

[0022]

Subsequently, the supply of TMGa was stopped, the temperature of the sapphire substrate 1 was raised to 1,150°C, and while keeping this temperature, the carrier gas, ammonia gas, H₂ containing TMA1 vapor, H₂ containing TMGa vapor, and H₂ containing biscyclopentadienylmagnesium (Cp2Mg) vapor were fed into the reaction chamber at 6 slm, 3 slm, 4.3 sccm, 5 sccm and 135 sccm, respectively, over 10 minutes. At this time, the amounts in mol of TMA1, TMGa and Cp2Mg supplied were 2.3×10^{-6} mol/min, 1.5×10^{-5} mol/min and 1.1×10^{-4} mol/min, respectively.

During this process, a p-type AlGaN layer 35 having a thickness of about 70 nm and a carrier concentration of $1 \times 10^{17}/\text{cm}^3$ was formed.

[0023]

Thereafter, the supply of TMA1, TMGa and Cp2Mg was stopped, the temperature of the sapphire substrate 1 was

lowered to 1,100°C, and while keeping this temperature, the carrier gas, ammonia gas, H₂ containing TMGa vapor, and H₂ containing Cp2Mg vapor were fed into the reaction chamber at 6 slm, 2.5 slm, 15 sccm and 135 sccm, respectively, over 10 minutes.

At this time, the amounts in mol of TMGa and Cp2Mg were 5.7×10^{-5} mol/min and 1.1×10^{-4} mol/min, respectively.

During this process, a p-type GaN layer 36 having a thickness of about 300 nm and a carrier concentration of $3 \times 10^{17}/\text{cm}^3$ was formed.

[0024]

The thus-obtained epitaxial wafer was taken out from the reaction chamber and then, n-electrode 37 and p-electrode 38 were provided on the n-type GaN layer 32 and p-type GaN layer 36, respectively, using a known device formation technique.

The device obtained was measured on the brightness when light was emitted by passing a current of 20 mA in the forward direction between the n-electrode 37 and the p-electrode 38 of the device. The results obtained are shown in Table 1.

Also, the water concentration of the liquid phase ammonia in the charging container (at the initiation of test) is shown in Table 1.

[0025]

(Test Examples 2 to 7)

GaN-type compound semiconductor devices were manufactured in the same manner as in Test Example 1 except that the water concentration of ammonia (at the initiation of test) used by filling it in a charging container was changed as shown in Table 1.

The thus-obtained GaN-type compound semiconductor devices were measured on the brightness at the light emission and the results are shown together in Table 1.

[0026]

The water concentration of the liquid phase ammonia was determined by sampling and vaporizing the liquid phase ammonia in the charging container and measuring the water content in the gas obtained using FT-IR (MAGNA560, manufactured by NICOLET).

The water concentration of the liquid phase ammonia shown here is a water content in terms of volume percent of part per million (vol ppm) in the gas obtained by sampling and vaporizing the liquid phase ammonia.

[0027]

[Table 1]

	Water Concentration in Liquid Phase (vol ppm)	Brightness (cd)
Test Example 1	1.0	0.1
Test Example 2	0.8	0.5
Test Example 3	0.5	1.5
Test Example 4	0.4	2.1
Test Example 5	0.2	2.6
Test Example 6	0.1	2.8
Test Example 7	0.01	3.0

[0028]

It is seen from Table 1 that devices manufactured by the method of using ammonia in which the liquid phase ammonia has a water concentration of 0.5 vol ppm or less, have excellent light emitting properties.

In particular, devices manufactured by the method of using ammonia in which the above-described water concentration is 0.4 vol ppm or less exhibit high brightness of 2 cd or more and furthermore, devices manufactured using ammonia in which the above-described water concentration is 0.2 vol ppm or less have still more excellent light emitting properties.

[0029]

[Effects of the Invention]

As described in the foregoing, according to the present invention, a GaN-type compound semiconductor having excellent light emitting properties such as brightness can be obtained without fail and the production yield can be improved.

[BRIEF DESCRIPTION OF DRAWINGS]

[Fig. 1]

Fig. 1 is a schematic constitutional view showing a production apparatus suitably used for implementing one embodiment of the method for manufacturing a GaN-type compound semiconductor according to the present invention.

[Fig. 2]

Fig. 2 is a schematic constitutional view showing an ammonia charging container for use in the production apparatus of Fig. 1.

[Fig. 3]

Fig. 3 is a partial cross section showing an example of a GaN-type compound semiconductor device.

[Fig. 4]

Fig. 4 is a partial cross section showing an example of a GaN-type compound semiconductor device manufactured by one embodiment of the method for manufacturing a GaN-type compound semiconductor according to the present invention.

[Description of Numerical References]

1 ... sapphire substrate, 2 ... buffer layer, 3 ... n-type clad layer, 4 ... active layer, 5 ... p-type clad layer, 11 ... reaction chamber, 18 ... charging container, 31 ... buffer layer, 32 ... n-type GaN layer, 33 ... InGaN active layer, 34 ... GaN layer, 35 ... p-type AlGaN layer, and 36 ... p-type GaN layer.

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a method for manufacturing a GaN-type compound semiconductor, where a GaN-type compound semiconductor having excellent light emitting properties can be manufactured without fail.

[MEANS TO SOLVE THE PROBLEM]

Ammonia for use in the manufacture of a GaN-type compound semiconductor, filled in a charging container 18 such that at least a part of the ammonia is liquid and the liquid phase ammonia has a water concentration determined by a Fourier-transform infrared spectroscopy (FT-IR) of 0.5 vol ppm or less, is introduced in the gaseous state into a reaction chamber 11 housing therein a substrate 1, and a layer comprising a GaN-type compound started from this ammonia is formed on the substrate 1.

[SELECTED DRAWING] Fig. 1